

AD-A088 608

MASSACHUSETTS INST OF TECH CAMBRIDGE DEPT OF CHEMISTRY F/6 7/8
PHOTOCHEMISTRY OF COBALT CARBONYL COMPLEXES HAVING A COBALT-SIL--ETC(U)
AUG 80 C L REICHEL, M S WRIGHTON N00014-75-C-0880

UNCLASSIFIED

TR-21

NL

1 of 1
608 608



END

DATE

FILED

10-80

DTIC

UNCLASSIFIED

LEVEL II

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

AD A088608

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ONR-TR-21	2. GOVT ACCESSION NO. AD-A088608	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Photochemistry of Cobalt Carbonyl Complexes Having a Cobalt-Silicon Bond and Its Importance in Activation of Catalysis		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report
7. AUTHOR(s) Carol L. Reichel and Mark S. Wrighton		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Massachusetts Institute of Technology Cambridge, MA 02139		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-0880
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, VA 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-051-579
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE August 22, 1980
		13. NUMBER OF PAGES 22
		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; reproduction is permitted for any purpose of the United States Government; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Distribution of this document is unlimited.		
18. SUPPLEMENTARY NOTES Prepared and accepted for publication in <u>Inorganic Chemistry</u> .		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Photochemistry, catalysis, metal carbonyls, photocatalytic activity, hydrosilation.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Photochemistry of $R_3SiCo(CO)_4$ ($R = Et, Ph$) in hydrocarbon solvents shows that the dominant primary excited state process is loss of CO, not cleavage of the Si-Co bond. The 366 nm quantum yield for CO substitution by $P(OPh)_3$ is 0.28 \pm 0.05 to give $R_3SiCo(CO)_3P(OPh)_3$. Irradiation of $R_3SiCo(CO)_4$ in the presence of 0.1 M $HSiR'_3$ gives $R'_3SiCo(CO)_4$ with a quantum yield nearly the same as that for CO substitution by $P(OPh)_3$; irradiation of $Ph_3SiCo(CO)_4$ in the presence of 0.1 M $HSiEt_3$ and 0.3 M $P(OPh)_3$ yields only $Ph_3SiCo(CO)_3P(OPh)_3$, not		

DDC FILE COPY

DD FORM 1473
1 JAN 73EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

(over)

DTIC
ELECTE

SEP 3 1980

083
0829
0829

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

$\text{Et}_3\text{SiCo}(\text{CO})_3\text{P}(\text{OPh})_3$. Irradiation of $\text{R}_3\text{SiCo}(\text{CO})_4$ in the presence of 1-pentene first gives $\text{R}_3\text{SiCo}(\text{CO})_3(\text{alkene})$, but the dominant Co-containing material is ultimately a mixture $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$ at 25°C . For $\text{R}=\text{Et}$, the dominant Si-containing products have been determined to be isomers of $(\text{pentenyl})\text{SiEt}_3$. The quantum yield for reaction of $\text{Et}_3\text{SiCo}(\text{CO})_4$ with 1-pentene ($\phi = 0.23$) is significantly higher than the reaction quantum yield for $\text{Et}_3\text{SiCo}(\text{CO})_4$ in isooctane ($\phi = 0.04$) solution where mixtures of $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$ are the photoproducts. Irradiation of $\text{R}_3\text{SiCo}(\text{CO})_4$ in the presence of 1-pentene/ HSiEt_3 (1/1 mole ratio) yields catalytic alkene isomerization and hydrosilation. Thermal catalysis (25°C) of 1-pentene hydrosilation by HSiEt_3 using $\text{Co}_2(\text{CO})_8$ yields infrared detectable $\text{Et}_3\text{SiCo}(\text{CO})_4$. The $\text{Et}_3\text{SiCo}(\text{CO})_4$ does not catalyze thermal reaction at 25°C at a rate comparable to that initially observed using $\text{Co}_2(\text{CO})_8$. Regeneration of catalytic activity in the $\text{Co}_2(\text{CO})_8$ /1-pentene/ HSiEt_3 system can be accomplished photochemically by exciting the $\text{Et}_3\text{SiCo}(\text{CO})_4$ species.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Accession For	
1. IS GFW&I	<input checked="checked" type="checkbox"/>
2. TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or special
A	

OFFICE OF NAVAL RESEARCH

Contract N00014-75-C-0880

Task No. NR 051-579

TECHNICAL REPORT NO. 21

PHOTOCHEMISTRY OF COBALT CARBONYL COMPLEXES HAVING
A COBALT-SILICON BOND AND ITS IMPORTANCE IN
ACTIVATION OF CATALYSIS

by

Carol L. Reichel and Mark S. Wrighton
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Prepared for Publication

in

INORGANIC CHEMISTRY

August 22, 1980

Reproduction in whole or in part is permitted for any purpose of the United States Government.

This document has been approved for public release and sale; its distribution is unlimited.

DTIC
ELECTE
SEP 3 1980
S D

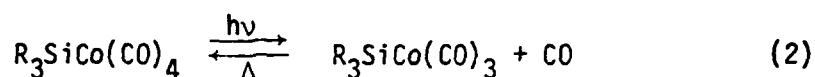
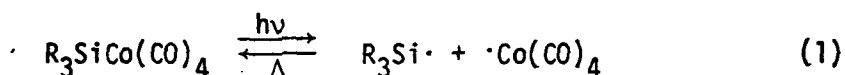
Contribution from Department of Chemistry,
Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139

Photochemistry of Cobalt Carbonyl Complexes Having a Cobalt-Silicon Bond
and Its Importance in Activation of Catalysis

Carol L. Reichel and Mark S. Wrighton*

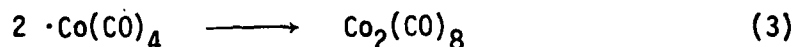
*To whom to address correspondence should be addressed.

We wish to report results of experiments that establish the relative importance of photochemical cleavage of the Co-Si bond vs. the dissociative loss of CO in $R_3SiCo(CO)_4$, equation (1) vs. (2). We recently showed¹ that

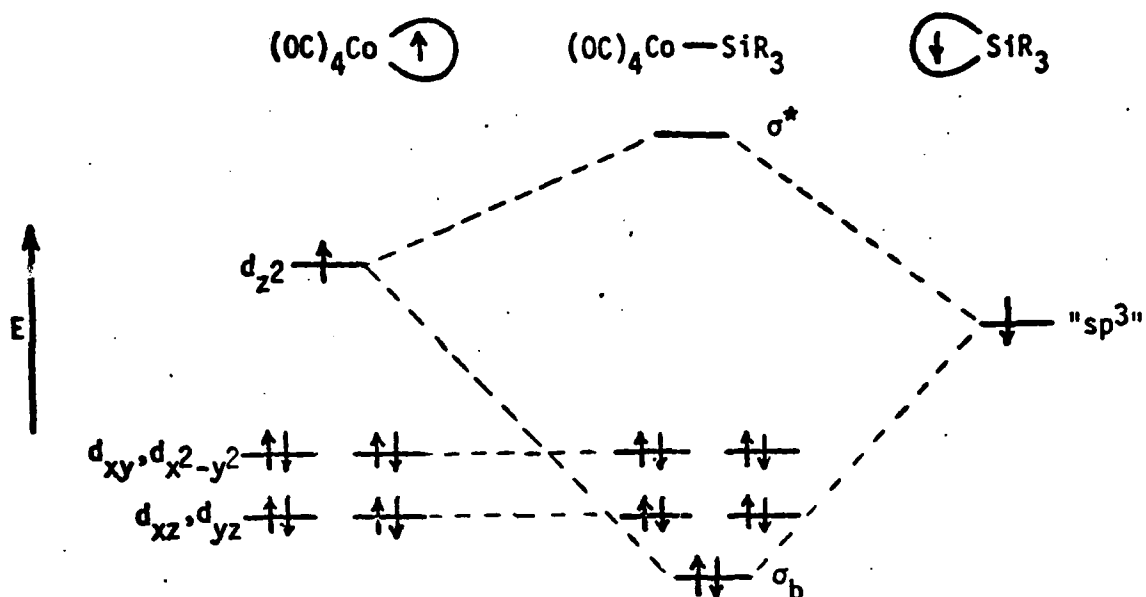


photogeneration of 17-valence electron, Co-centered radicals can lead to catalysis of alkene isomerization, hydrosilation, and hydrogenation.

Reaction of $R_3SiCo(CO)_4$ according to equation (1) is of interest in that the 17-valence electron radical $\cdot Co(CO)_4$ could effect the same alkene/ $HSiR_3$ reactions known² to be catalyzed by $Co_2(CO)_8$. It is believed that $R_3SiCo(CO)_4$ represents the ultimate fate of Co in the $Co_2(CO)_8$ catalyzed hydrosilation reaction and that it is not an active thermal catalyst at the temperatures that can be used for $Co_2(CO)_8$.² We thus wondered whether the $Co_2(CO)_8$ catalyst could be regenerated from irradiation of $R_3SiCo(CO)_4$ according to equations (1) and (3).



The relative importance of the two photoreactions represented by equations (1) and (2) is of fundamental interest, since there is considerable ambiguity concerning the importance of primary photogeneration of 17-valence electron vs. 16-valence electron fragments from coordinatively saturated, 18-valence electron species having both 2- and 1-electron donor ligands.³ For $R_3SiCo(CO)_4$ the orbital diagram in Scheme I is appropriate,⁴ and it is apparent that all lowest excited states involve population of $\sigma^*(d_{z^2})$



Scheme I. One-electron orbital diagram for $R_3SiCo(CO)_4$.

resulting in weakening of the σ -bonding between Co and all of the five ligands.

Experimental Section

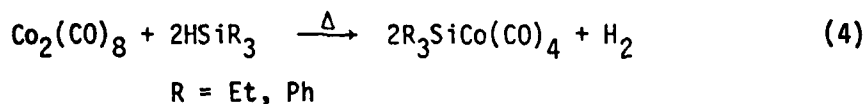
Infrared spectra were taken on a Perkin-Elmer Model 180 grating spectrophotometer in matched 1.0 mm or 0.1 mm pathlength amalgam sealed NaCl cells. Low temperature spectra were taken using a Cyrogenics Technology, Inc. Spectrim II cryocooler in conjunction with the spectrophotometer; a 1.1 mm pathlength uncompensated CaF_2 cell was constructed to interface with the cold head. Electronic spectra were taken on a Varian Associates Cary Model 17 uv-vis-nir spectrophotometer, in 1.0 cm quartz or 1.3 cm Pyrex cells. Gas-liquid chromatography was performed on a Varian Associates Model 1440 or 2440 gas chromatograph equipped with flame ionization detectors and interfaced with either a Hewlett-Packard model 3370S electronic recording integrator or a Varian model A25 strip chart recorder. Hydrocarbon analyses (against internal standard n-hexane) were carried out on columns of 20% propylene carbonate on Chromasorb P (Johns-Manville), 30" x 1/8", 20°C, hydrosilation products were analyzed (against internal standard n-decane) on columns of 20% β,β' -oxydepropionitrile on Gaschrom Q (Applied Science Laboratories, 1/8" x 30', 60°C). Organic products of the photolyses of $\text{Ph}_3\text{SiCo}(\text{CO})_4$ in pentene or isooctane were separated on columns of 1.5% OV-101 on Chromosorb P (1/8" x 5", 120-250°C, programmed at 10-20°C/min.) Nuclear magnetic resonance spectra were obtained with a Hitachi-Perkin Elmer R-24B or Varian T-60 spectrometer (^1H , 60 MHz) or with a Jeolco FX-90Q spectrometer (^1H , 90 MHz). Mass spectra were obtained on a Varian MAT 44 spectrometer, interfaced with a Varian series 1400 gas chromatograph for GC/MS.

All air-sensitive organometallic compounds were handled under an argon atmosphere by conventional Schlenk techniques, or under an atmosphere of prepurified nitrogen in a Vacuum Atmospheres Dri-Lab glove box. Photosensitive solutions were handled under red safelights or in the dark. $\text{Co}_2(\text{CO})_8$ (ROC/RIC, Strem) and $\text{P}(\text{OPh})_3$ (Strem) were used as received. PPh_3 (Aldrich) and

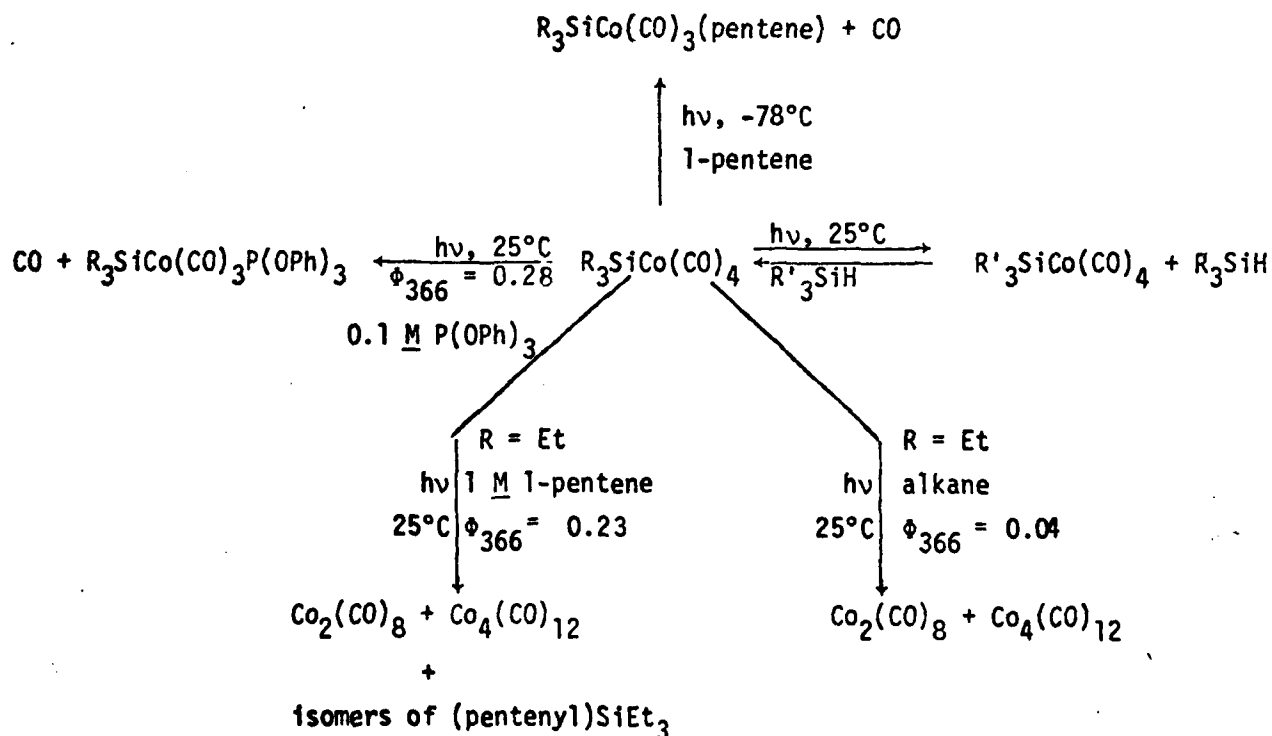
HSiPh_3 (Petrarch) were recrystallized from ethanol and pentane, respectively, before use. Alkenes (99%, PCR or Phillips Chemical Company) were passed through activated alumina (MC&B chromatographic grade, 80-325 mesh) prior to use and stored in amber bottles at 4°C. Triethylsilane (Petrarch) was treated similarly. $\text{Co}_4(\text{CO})_{12}$ was prepared by heating $\text{Co}_2(\text{CO})_8$ under N_2 in isooctane at 80-90°C for 12 hrs, filtering off the product and recrystallizing from benzene/isooctane under N_2 . $\text{R}_3\text{SiCo}(\text{CO})_4$ (R = Et, Ph) were prepared by the literature method of Chalk and Harrod.⁵ Solvents were reagent grade or better; isooctane was spectrophotometric grade. For work with air- or water-sensitive species solvents were distilled under argon from appropriate drying agents.

Solutions for irradiation were hermetically sealed into 13 mm o.d. pyrex ampules after at least four freeze-pump-thaw degassing cycles under high vacuum. Alternatively, the organometallic was added, in the glove box to previously degassed solvent, the mixture transferred to 13 mm o.d. pyrex tubes with ground glass joint tops and sealed with rubber septa. Irradiation samples were generally 1-4 ml in volume, $\sim 10^{-3}\text{M}$ in metal carbonyl for catalysis and 10^{-2} - 10^{-4}M for spectral studies. Light intensities were determined by ferrioxalate actinometry.⁶ Near-ultraviolet irradiation was generated by two General Electric Blacklites ($\lambda_{\text{max}} = 355 \pm 20 \text{ nm}$, $I \sim 2 \times 10^{-6} \text{ ein/min}$) or a high-pressure mercury arc lamp (Bausch and Lomb, model SP200, 200 W) with an 18 cm water filter to remove infrared radiation. Monochromatic light was supplied by medium-pressure mercury arc lamps (Hanovia, 450 W or 550 W) filtered with Corning glass filters to isolate the desired emission ($I \sim 10^{-7} \text{ ein/min}$ with associated merry-go-round). 254 nm irradiation was supplied by a UV-Products low-pressure mercury arc lamp.

The complexes $R_3SiCo(CO)_4$ ($R = Et, Ph$) were synthesized and purified according to the literature procedures,⁵ equation (4). These complexes are



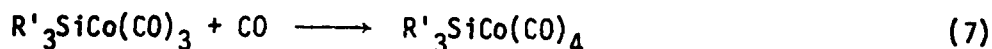
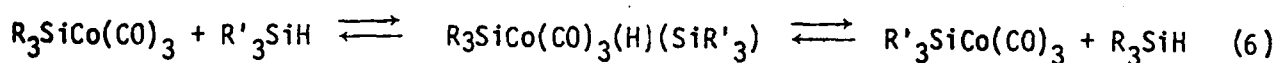
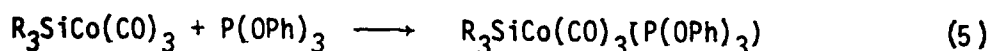
thermally inert at 25°C in deoxygenated hydrocarbon solutions containing 1-pentene, $HSiR_3$, $P(OPh)_3$ or mixtures of these reagents. However, these complexes are photosensitive upon near ultraviolet irradiation. Scheme II summarizes the photochemistry under various conditions. The data support the conclusion that dissociative loss of CO, equation (2), is the main result of photo-excitation of $R_3SiCo(CO)_4$. However, small quantum yields for $Co_2(CO)_8$ and some $Co_4(CO)_{12}$ formation in alkane solution are found and the chemical yield of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ are >90% based on $R_3SiCo(CO)_4$ consumed. In the presence of 1.0 M 1-pentene at 25°C the quantum yield for $Co_2(CO)_8$ formation increases markedly, but at -78°C the photoreaction leads to no detectable $Co_2(CO)_8$. At -78°C infrared spectral changes accompanying 355 nm



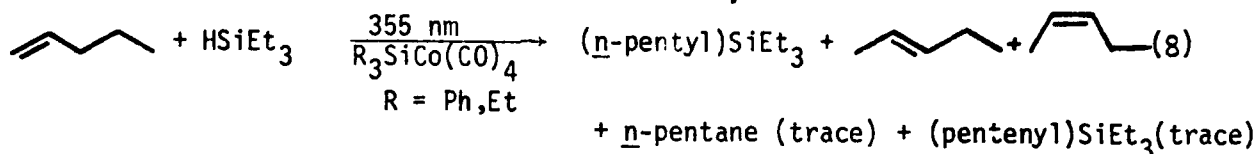
Scheme II: Photochemistry of $R_3SiCo(CO)_4$.

irradiation in 1.0 M 1-pentene in isooctane are consistent with the formation of $R_3SiCo(CO)_3(\text{pentene})$ ($R = Et$, $\nu_{CO} = 1966 \text{ sh}, 1959 \text{ cm}^{-1}$; $R = Ph$, $\nu_{CO} = 1977 \text{ sh}, 1970 \text{ cm}^{-1}$). Addition of $P(OPh)_3$ /isooctane in the dark to the irradiated solution at -78°C followed by warmup to 25°C and infrared analysis reveals the presence of $R_3SiCo(CO)_3P(OPh)_3$, evidencing photogeneration of a labile species at -78°C .⁷ Warmup of $Et_3SiCo(CO)_3(\text{pentene})$ - containing solutions in the absence of added $P(OPh)_3$ gives regeneration of $Et_3SiCo(CO)_4$ and a significant amount of $Co_4(CO)_{12}$. The low temperature irradiations appear to rule out chemistry according to equation (1) as the major pathway to $Co_2(CO)_8$. At 25°C in the presence of 1-pentene, irradiation of $Et_3SiCo(CO)_4$ leads to formation of isomers of $(\text{pentenyl})SiEt_3$ as the dominant Si-containing product,⁸ though initial infrared spectral changes are consistent with formation of $Et_3SiCo(CO)_3(\text{pentene})$.

Consistent with dissociative loss of CO as the major primary photoreaction, we find high quantum efficiency ($\phi \sim 0.28$) for the substitution of CO by $P(OPh)_3$. Irradiation of $R_3SiCo(CO)_4$ in the presence of R'_3SiH , Figure 1, results in clean formation of $R'_3SiCo(CO)_4$ with good quantum yield; irradiation in the presence of 0.1 M R'_3SiH and 0.3 M $P(OPh)_3$ only yields $R_3SiCo(CO)_3P(OPh)_3$. The rationale for these results is given by equations (2) and (5)-(7), indicating competitive capture of the 16^- species by $P(OPh)_3$ or $HSiR'_3$.



With respect to catalysis, we find that irradiation of $R_3SiCo(CO)_4$ in the presence of 1-pentene/ $HSiEt_3$ does lead to the isomerization and hydrosilation of the 1-pentene, equation (8). Only traces of $(\text{pentenyl})SiEt_3$



products are found. Data for the photocatalyzed reactions are given in the Table. The $\text{R}_3\text{SiCo(CO)}_4$ species lead to extensive pentene isomerization prior to significant extent conversion to $(\text{n-pentyl})\text{SiEt}_3$. Of the order of 10^3 molecules of $(\text{n-pentyl})\text{SiEt}_3$ have been observed per molecule of $\text{R}_3\text{SiCo(CO)}_4$ initially added and the turnover rate for formation of this product is of the order of 25 h^{-1} at the light intensity used to generate data given in the Table. Higher light intensities have yielded observed turnover rates for the reaction of $\sim 250 \text{ h}^{-1}$. Thermal activity of $\text{R}_3\text{SiCo(CO)}_4$ at 25°C for $(\text{n-pentyl})\text{SiEt}_3$ formation is low on the scale of light induced activity, but significant isomerization is detectable in thermal controls. The Table also shows data that reveal that when thermal catalytic activity of $\text{Co}_2(\text{CO})_8$ is over, catalytic activity can be revived by irradiation. These representative photoactivation data show an additional ~ 100 turnovers per Co after the catalytic activity for the $\text{Co}_2(\text{CO})_8$ is over. While it is tempting to conclude that the same catalyst is generated from irradiation of $\text{Et}_3\text{SiCo(CO)}_4$ as from $\text{Co}_2(\text{CO})_8$ in the dark, we cannot yet unequivocally make this conclusion. We do find that the $(\text{n-pentyl})\text{SiEt}_3$ is the dominant detectable Si-containing product in both cases. Thus, it would appear that the $\text{Co}_2(\text{CO})_8$ activity can be prolonged by irradiation; infrared analysis of the $\text{Co}_2(\text{CO})_8$ /pentene/ HSiEt_3 solution when thermal reaction has stopped shows $\text{Et}_3\text{SiCo(CO)}_4$ to account for $>80\%$ of the Co. The photoreaction of $\text{Et}_3\text{SiCo(CO)}_4$ in pentene to yield $(\text{pentenyl})\text{SiEt}_3$ (*vide supra*) provides a pathway to an active catalyst. The formation of $(\text{pentenyl})\text{SiEt}_3$ may occur by first forming $\text{Et}_3\text{SiCo(CO)}_3(\text{pentene})$ followed by insertion to yield $(\text{pentenylSiEt}_3)\text{Co(CO)}_3$ which then rapidly gives β -hydrogen transfer to yield the substitution labile complex $(\text{pentenylSiEt}_3)\text{Co(CO)}_3\text{H}$. This hydride can then lose the $(\text{pentenyl})\text{SiEt}_3$ to leave behind the coordinatively

unsaturated HCo(CO)_3 that is very likely the active catalyst in the $\text{Co}_2(\text{CO})_8$ system.^{2,5} In addition to determining its role in forming the active catalyst here, further study of this photoreaction is being undertaken to gain insight into the possible mechanism in Fe(CO)_5 photocatalyzed reaction of HSiR_3 /1-pentene that gives substantial amounts of (pentenyl) SiR_3 as a catalysis product.^{8,9}

Acknowledgements. We thank the Office of Naval Research for partial support of this research and M.S.W. acknowledges support as a Dreyfus Teacher-Scholar grant recipient, 1975-1980. C.L.R. was supported during Spring, 1980 by a Fellowship with funds generously provided by Eastman Kodak Co.

References

1. Reichel, C.L.; Wrighton, M.S. J. Am. Chem. Soc., 1979, 101, 6769.
2. Harrod, J.F.; Chalk, A.J. "Organic Synthesis via Metal Carbonyls", Vol. 2, Pino, P.; Wender, I. eds., John Wiley & Sons, Inc.: New York, 1977; pp. 687-690.
3. (a) Geoffroy, G.L.; Wrighton, M.S. "Organometallic Photochemistry", Academic Press, Inc.: New York, 1979; (b) Severson, R.G.; Wojcicki, A. J. Organometal. Chem., 1978, 157, 173.
4. Photoelectron spectroscopy of $\text{H}_3\text{SiCo(CO)}_4$ shows the $3d_{x^2-y^2}$, d_{xy} and $3d_{xz}$, d_{yz} orbitals to be the highest occupied levels with the σ_b level more stable: Cradock, S.; Ebsworth, E.A.V.; Robertson, A. J. Chem. Soc., Dalton, 1973, 22.
5. Chalk, A.J.; Harrod, J.F. J. Am. Chem. Soc., 1967, 89, 1640.
6. Hatchard, C.G.; Parker, C.A. Proc. Roy. Soc. A, 1956, 235, 518.
7. These $\text{R}_3\text{SiCo(CO)}_3\text{P(OPh)}_3$ complexes have ir spectra in the CO region as follows: R = Et, 1969 sh, 1965 cm^{-1} ; R = Ph, 1980 sh, 1973 cm^{-1} in isooctane/1-pentene (1/1 by volume). These spectra are similar to those for the $\text{R}_3\text{SiCo(CO)}_3(\text{pentene})$ detected at -78°C consistent with a similar arrangement of the CO groups. The spectra accord well with those for $\text{R}_3\text{ECo(CO)}_3\text{L}$ complexes previously reported: Boyd, T.E.; Brown, T.L. Inorg. Chem., 1974, 13, 422.
8. The isomers have been characterized by GC and mass spectral analyses compared to authentic samples prepared previously: Schroeder, M.A.; Wrighton, M.S. J. Organometal. Chem., 1977, 128, 345.
9. (a) Austin, R.G.; Paonessa, R.S.; Giordano, P.J.; Wrighton, M.S. Adv. Chem. Ser., 1978, 168, 189; (b) Nesmeyanov, A.N.; Friedlina, R.K.; Chukovskaya, E.C.; Petrova, R.G.; Belyavsky, A.B. Tetrahedron, 1962, 17, 61; (c) Friedlina, R.K.; Chukovskaya, E.C.; Tsao, J.; Nesmeyanov, A.N.; Dokl. Akad. Nauk. SSSR, 1960, 132, 37.

Table. Photocatalyzed Reaction of 1-Pentene with HSiEt_3 .^a

Catalyst Precursor	1-Pentene/ SiEt_3	Irrdn Time	% Consumption of 1-Pentene	Product Analysis, %		
				n-pentane	t-2- c-2-pentene	(n-pentyl) SiEt_3
$\text{Ph}_3\text{SiCo}(\text{CO})_4$ ($1.79 \times 10^{-3}\text{M}$)	1.0 M/1.0M (in n-octane)	0 (39h thermal control) ^b	8	0	91	0
		1	26	<1	90	7
		4.7	96	<1	64	16
		39	97	<1	57	13
$\text{Ph}_3\text{SiCo}(\text{CO})_4$ ($1.79 \times 10^{-3}\text{M}$)	3.3M/3.3M (neat)	1	7.9	1	81	14
		4.7	97	<1	79	14
		39	>97	<1	38	9
$\text{Et}_3\text{SiCo}(\text{CO})_3$ ($1.79 \times 10^{-3}\text{M}$)	3.3M/3.3M (neat)	4.7	97	<1	79	14
		39	>97	1	32	8
$\text{Co}_2(\text{CO})_8$ ($2 \times 10^{-2}\text{M}$)	3.3M/3.3M (neat)	0 (10h thermal) ^c	>97	-----	-----	23
		15 after 10h thermal ^d	>97	-----	-----	35
$\text{Co}_2(\text{CO})_8$ ($2 \times 10^{-3}\text{M}$)	3.3M/3.3M (neat)	0 (17h thermal) ^c	>97	-----	-----	15
		10h after 17h thermal ^{d,e}	>97	-----	-----	28

^a Irradiation of 1.0 cc deoxygenated samples in Pyrex ampules using 355 ± 20 nm light at 2×10^{-6} ein/min and at 25°C . Solutions were analyzed by GC and quantitated by using internal standards n-hexane for determination of C_5 's and n-decane for (pentyl) SiEt_3 .

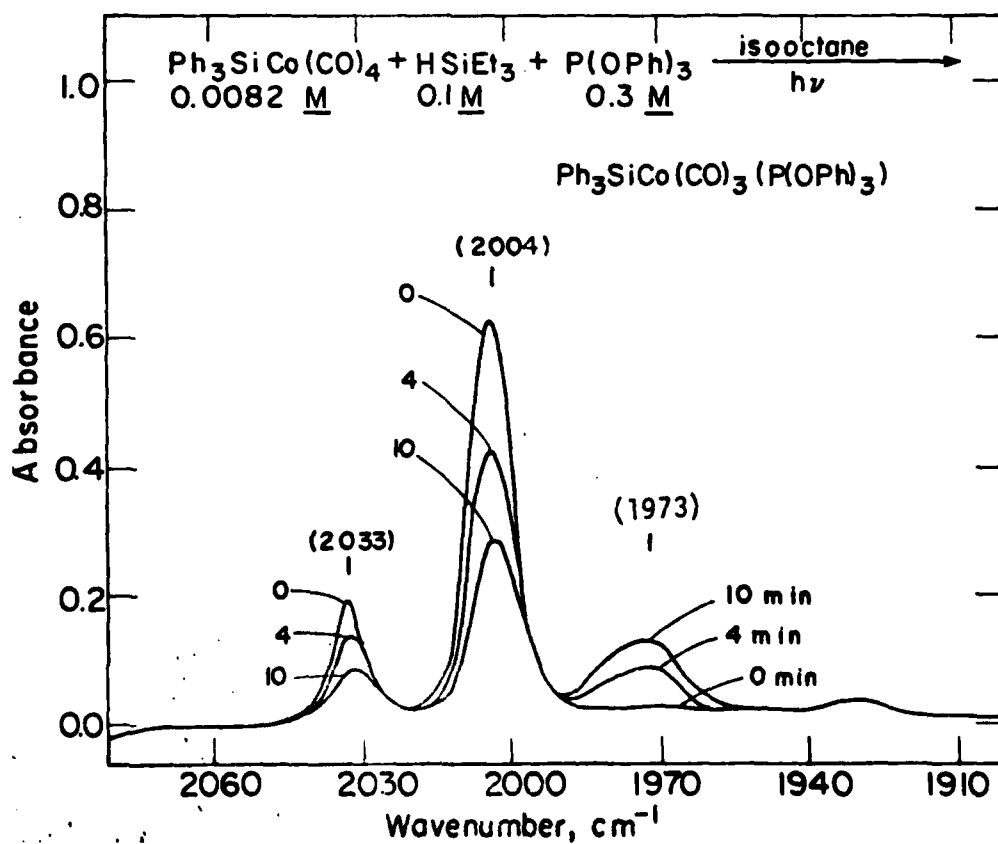
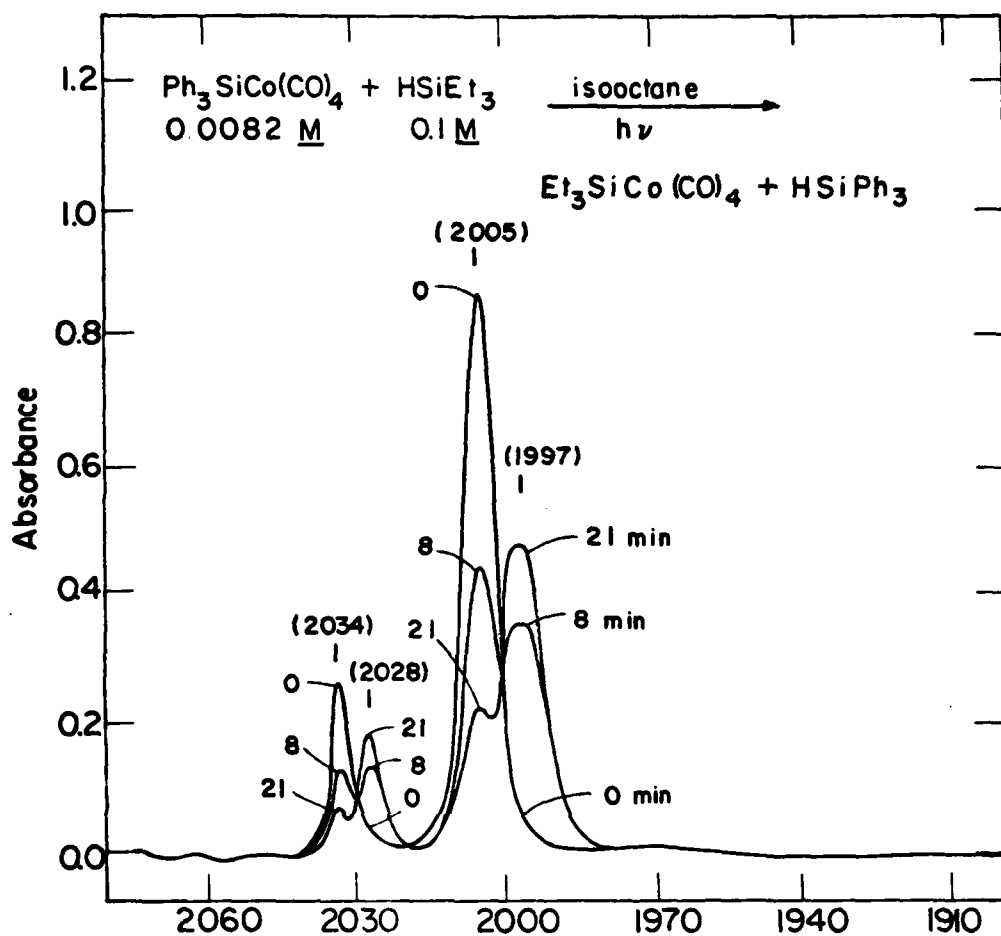
^b 39 h under same conditions except not irradiated.

^c This represents a point in the reaction when there is no further detectable activity.

^d In these experiments the irradiation was not started until thermal activity ceased. The species irradiated is principally $\text{Et}_3\text{SiCo}(\text{CO})_4$ as detected by infrared.

^e A higher light intensity was used in this experiment.

Figure Caption. Comparison of photochemistry of $\text{Ph}_3\text{SiCo(CO)}_4$ in the presence of HSiEt_3 only (a) and HSiEt_3 and P(OPh)_3 (b). Irradiation of the 25°C deoxygenated solutions is at 355 nm (± 20 nm). Note that quantum yield for disappearance of $\text{Ph}_3\text{SiCo(CO)}_4$ is the same in both cases but that silane exchange occurs exclusively in (a) and P(OPh)_3 substitution occurs exclusively in (b), consistent with competitive capture of a $16e^-$ species by P(OPh)_3 or HSiEt_3 , equations (5) and (6) in text.



TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
ONR Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605	1	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Area Office Attn: Scientific Dept. 715 Broadway New York, New York 10003	1	Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
ONR Western Regional Office 1030 East Green Street Pasadena, California 91106	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
ONR Eastern/Central Regional Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
The Assistant Secretary of the Navy (RE&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

SP472-3/A3

472:GAN:716:ddc
78u472-608

TECHNICAL REPORT DISTRIBUTION LIST, GEN

No.
Copies

Dr. Rudolph J. Marcus
Office of Naval Research
Scientific Liaison Group
American Embassy
APO San Francisco 96503

1

Mr. James Kelley
DTNSRDC Code 2803
Annapolis, Maryland 21402

1

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. Paul Delahay Department of Chemistry New York University New York, New York 10003	1	Dr. P. J. Hendra Department of Chemistry University of Southampton Southampton SO9 5NH United Kingdom	1
Dr. E. Yeager Department of Chemistry Case Western Reserve University Cleveland, Ohio 44106	1	Dr. Sam Perone Department of Chemistry Purdue University West Lafayette, Indiana 47907	1
Dr. D. N. Bennion Department of Chemical Engineering Brigham Young University Provo, Utah 84602	1	Dr. Royce W. Murray Department of Chemistry University of North Carolina Chapel Hill, North Carolina 27514	1
Dr. R. A. Marcus Department of Chemistry California Institute of Technology Pasadena, California 91125	1	Naval Ocean Systems Center Attn: Technical Library San Diego, California 92152	1
Dr. J. J. Auburn Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. C. F. Mueller The Electrochemistry Branch Materials Division, Research & Technology Department Naval Surface Weapons Center White Oak Laboratory Silver Spring, Maryland 20910	1
Dr. Adam Heller Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. G. Goodman Globe-Union Incorporated 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1
Dr. T. Katan Lockheed Missiles & Space Co, Inc. P.O. Box 504 Sunnyvale, California 94088	1	Dr. J. Boechler Electrochimica Corporation Attention: Technical Library 2485 Charleston Road Mountain View, California 94040	1
Dr. Joseph Singer, Code 302-1 NASA-Lewis 21000 Brookpark Road Cleveland, Ohio 44135	1	Dr. P. P. Schmidt Department of Chemistry Oakland University Rochester, Michigan 48063	1
Dr. B. Brummer EIC Incorporated 55 Chapel Street Newton, Massachusetts 02158	1	Dr. H. Richtol Chemistry Department Rensselaer Polytechnic Institute Troy, New York 12181	1
Library P. R. Mallory and Company, Inc. Northwest Industrial Park Burlington, Massachusetts 01803	1		

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. A. B. Ellis Chemistry Department University of Wisconsin Madison, Wisconsin 53706	1	Dr. R. P. Van Duyne Department of Chemistry Northwestern University Evanston, Illinois 60201	1
Dr. M. Wrighton Chemistry Department Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Dr. B. Stanley Pons Department of Chemistry University of Alberta Edmonton, Alberta CANADA T6G 2G2	1
Larry E. Plew Naval Weapons Support Center Code 30736, Building 2906 Crane, Indiana 47522	1	Dr. Michael J. Weaver Department of Chemistry Michigan State University East Lansing, Michigan 48824	1
S. Rubv DOE (STOR) 600 E Street Washington, D.C. 20545	1	Dr. R. David Rauh EIC Corporation 55 Chabel Street Newton, Massachusetts 02158	1
Dr. Aaron Wold Brown University Department of Chemistry Providence, Rhode Island 02192	1	Dr. J. David Margerum Research Laboratories Division Hughes Aircraft Company 3011 Malibu Canyon Road Malibu, California 90265	1
Dr. R. C. Chudacek McGraw-Edison Company Edison Battery Division Post Office Box 28 Bloomfield, New Jersey 07003	1	Dr. Martin Fleischmann Department of Chemistry University of Southampton Southampton 509 5NH England	1
Dr. A. J. Bard University of Texas Department of Chemistry Austin, Texas 78712	1	Dr. Janet Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. M. M. Nicholson Electronics Research Center Rockwell International 3370 Miraloma Avenue Anaheim, California	1	Dr. R. A. Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. Donald W. Ernst Naval Surface Weapons Center Code R-33 White Oak Laboratory Silver Spring, Maryland 20910	1	Mr. James R. Moden Naval Underwater Systems Center Code 3632 Newport, Rhode Island 02840	1

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. R. Nowak Naval Research Laboratory Code 6130 Washington, D.C. 20375	1	Dr. John Kincaid Department of the Navy Strategic Systems Project Office Room 901 Washington, DC 20376	1
Dr. John F. Houlihan Shenango Valley Campus Pennsylvania State University Sharon, Pennsylvania 16146	1	M. L. Robertson Manager, Electrochemical Power Sonics Division Naval Weapons Support Center Crane, Indiana 47522	1
Dr. M. G. Sceats Department of Chemistry University of Rochester Rochester, New York 14627	1	Dr. Elton Cairns Energy & Environment Division Lawrence Berkeley Laboratory University of California Berkeley, California 94720	1
Dr. D. F. Shriver Department of Chemistry Northwestern University Evanston, Illinois 60201	1	Dr. Bernard Spielvogel U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709	1
Dr. D. H. Whitmore Department of Materials Science Northwestern University Evanston, Illinois 60201	1	Dr. Denton Elliott Air Force Office of Scientific Research Bldg. 104 Bolling AFB Washington, DC 20332	1
Dr. Alan Bewick Department of Chemistry The University Southampton, SO9 5NH England	1		
Dr. A. Himy NAVSEA-5433 NC #4 2541 Jefferson Davis Highway Arlington, Virginia 20362	1		

TECHNICAL REPORT DISTRIBUTION LIST, 051A

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. M. A. El-Sayed Department of Chemistry University of California, Los Angeles Los Angeles, California 90024	1	Dr. M. Rauhut Chemical Research Division American Cyanamid Company Bound Brook, New Jersey 08805	1
Dr. E. R. Bernstein Department of Chemistry Colorado State University Fort Collins, Colorado 80521	1	Dr. J. I. Zink Department of Chemistry University of California, Los Angeles Los Angeles, California 90024	1
Dr. C. A. Heller Naval Weapons Center Code 6059 China Lake, California 93555	1	Dr. D. Haarer IBM San Jose Research Center 5600 Cottle Road San Jose, California 95143	1
Dr. J. R. MacDonald Chemistry Division Naval Research Laboratory Code 6110 Washington, D.C. 20375	1	Dr. John Cooper Code 6130 Naval Research Laboratory Washington, D.C. 20375	1
Dr. G. B. Schuster Chemistry Department University of Illinois Urbana, Illinois 61801	1	Dr. William M. Jackson Department of Chemistry Howard University Washington, DC 20059	1
Dr. A. Adamson Department of Chemistry University of Southern California Los Angeles, California 90007	1	Dr. George E. Walraffen Department of Chemistry Howard University Washington, DC 20059	1
Dr. M. S. Wrighton Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1		